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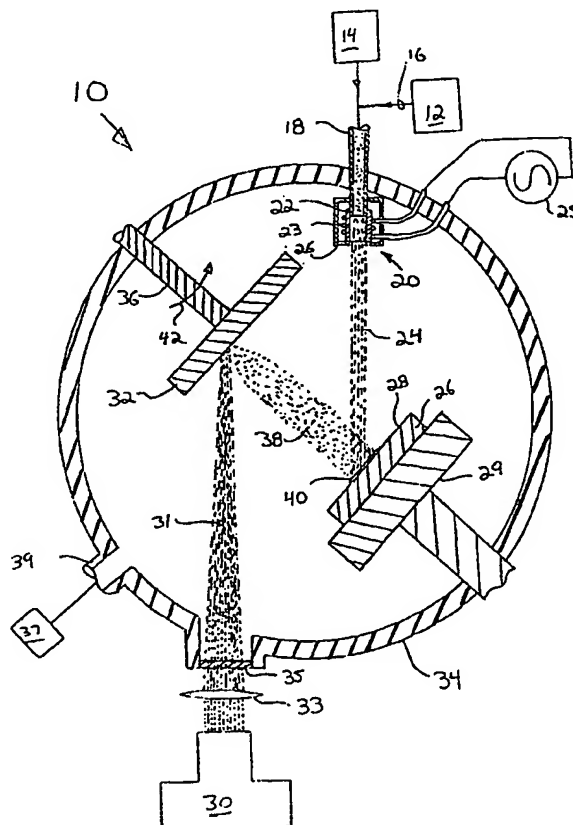
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(54) Title: **EXTENDED NITRIDE MATERIAL COMPRISING  $\beta$ -C<sub>3</sub>N<sub>4</sub>**

## (57) Abstract

An extended nitride material comprises  $\beta$ -C<sub>3</sub>N<sub>4</sub>. A method of forming an extended nitride material includes forming an atomic nitrogen source, forming an elemental reagent source and combining the atomic nitrogen and elemental reagent to form the extended nitride material. The elemental reagent is reactive with the atomic nitrogen of the atomic nitrogen source to form the extended nitride material. The apparatus of the invention can include, for example, a radio-frequency (rf) discharge nozzle for forming the atomic nitrogen source, such as an atomic nitrogen beam. The elemental reagent source can be formed by employing a pulsed laser to ablate a suitable target, such as a graphite target, to thereby form an ablation plume of elemental carbon. The ablation plume and the atomic nitrogen beam combine and cause the elemental carbon reagent and the atomic nitrogen to react and form the extended nitride material. The extended nitride material can accumulate as a film on a suitable substrate, such as Si(100) or polycrystalline nickel.



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EXTENDED NITRIDE MATERIAL COMPRISING  $\beta$ -C<sub>3</sub>N<sub>4</sub>Background of the Invention

There is a great demand in industry for new materials. Of especial importance is development of materials which have extreme physical properties that can substitute for expensive known materials. Diamond, for example, is industrially useful because it is the hardest known material. However, even synthetically-formed diamond is very expensive.

At least one material has been identified which, hypothetically, would have a bulk modulus (and corresponding hardness) comparable to that of diamond. This material, like diamond, would be an extended solid, but would have an empirical formula of  $\beta$ -C<sub>3</sub>N<sub>4</sub> and could be a superior alternative to many known materials, including diamond. However,  $\beta$ -C<sub>3</sub>N<sub>4</sub> would be metastable, as are other similar nitride materials.

Examples of failed attempts to form  $\beta$ -C<sub>3</sub>N<sub>4</sub> have included plasma decomposition of methane and nitrogen gas, and pyrolytic decomposition of C-N-H type organic compounds. Both methods have formed only C-N-H type solids and have not yielded any evidence of  $\beta$ -C<sub>3</sub>N<sub>4</sub>. It has been suggested that the relative stability of hydrocarbon and N-H type reaction products under the conditions of the plasma decomposition and pyrolytic decomposition methods have precluded formation of  $\beta$ -C<sub>3</sub>N<sub>4</sub>.

Another example of an attempt to form  $\beta$ -C<sub>3</sub>N<sub>4</sub> has been shock wave compression of C-N-H type precursors. Although diamond has been formed by this method, there has been no evidence of  $\beta$ -C<sub>3</sub>N<sub>4</sub>.

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Summary of the Invention

The present invention relates to an extended nitride material wherein at least a portion of the material has an empirical formula of  $\beta\text{-C}_3\text{N}_4$ , and to a method and apparatus of forming an extended nitride material, such as  $\beta\text{-C}_3\text{N}_4$ .

The method includes forming an atomic nitrogen source and an elemental reagent source. The elemental reagent source includes an elemental reagent, such as carbon, boron, silicon or titanium, which is reactive with atomic nitrogen of the atomic nitrogen source to form the extended nitride material. The atomic nitrogen and the elemental reagent are combined to cause the atomic nitrogen and the elemental reagent to react and form the extended nitride material.

The apparatus includes means for forming an atomic nitrogen source and means for forming an elemental reagent source, whereby atomic nitrogen and the elemental reagent can react to form the extended nitride material.

Advantages of the present invention include, for example, the ability to form metastable nitride materials. Among the materials that can be formed are those, such as  $\beta\text{-C}_3\text{N}_4$ , which have not been successfully formed by conventional methods. Further, the materials formed can have superior physical properties and can be employed advantageously as substitutes for relatively expensive existing materials and for materials formed by known methods.

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Brief Description of the Drawings

Figure 1 is a plan view of one embodiment of the apparatus of the present invention.

Figures 2a-2c are a series of plots of Rutherford backscattering spectra recorded on 3  $\mu\text{m}$  thick C-N films formed by the method of the present invention using one, four, and twelve percent nitrogen gas in helium.

Figure 3 is an electron diffraction pattern recorded on material from a C-N film formed by the method of the present invention, wherein the film contained sixty percent carbon and forty percent nitrogen, and using an electron beam energy of about 120 keV.

Figure 4 is a Rutherford backscattering spectrum (RBS) acquired with a glancing angle geometry.

Detailed Description of the Invention

The features and other details of the method of the invention will now be more particularly described with reference to the accompanying drawings and pointed out in the claims. It will be understood that the particular embodiments of the invention are shown by way of illustration and not as limitations of the invention. The principle features of this invention can be employed in various embodiments without departing from the scope of the invention.

The present invention includes a method and apparatus for forming an extended nitride material. One embodiment of the apparatus of the invention is shown in Figure 1. Apparatus 10 of Figure 1 includes means for forming an atomic nitrogen source and means for forming an elemental reagent source which is

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reactive with atomic nitrogen of the atomic nitrogen source to form the extended nitride material.

Preferably, means for forming an atomic nitrogen source include nitrogen gas source 12 and inert gas source 14. An example of a suitable inert gas is helium. Conduits 16 and 18 extend from nitrogen gas source 12 and inert gas source 14, respectively, and intersect for combination of nitrogen and a suitable inert gas in conduit 18. Conduit 18 extends to radio-frequency discharge source 20. In a particularly preferred embodiment, radio frequency discharge 20 source includes aluminum oxide ( $\text{Al}_2\text{O}_3$ ) nozzle 22 and coil 23. Coil 23 is connected to a suitable power source 25. Housing 26 extends about nozzle 22 and coil 23. An example of a suitable housing is a housing formed of copper (Cu). Radio frequency discharge source 20 is suitable for directing an atomic nitrogen source, such as atomic nitrogen beam 24 formed by exposure of nitrogen gas to radio-frequency discharge at radio-frequency discharge source 20, to substrate 26 at surface 28.

Substrate 26 is mounted on supporting heater 29. Examples of suitable substrates include Si(100), polycrystalline nickel, other suitable metals, etc. Suitable metal substrates can be at least one component of an article of manufacture, such as a cutting tool for material fabrication, or a bearing surface.

In one embodiment, means for forming the elemental reagent source include laser 30, which can form laser beam 31, and target 32. Examples of suitable lasers include Nd:YAG and excimer lasers. Lens 33 is positioned between laser 30 and window 35 of vessel 34. Lens 33 is suitable for focusing laser beam 31 onto

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target 32. Target 32 is formed of a suitable material for forming a plume of elemental reagent which, when combined with the atomic nitrogen of the atomic nitrogen source, will react with the atomic nitrogen to form the extended nitride material. Examples of suitable targets include carbon-nitride, graphite, silicon, boron and titanium targets. A preferred target is graphite. A particularly preferred target is oriented pyrolytical graphite. Target 32 is mounted on rotating support 36.

Target 32 and substrate 28 are sealed within vessel 34. Vacuum source 37 extends from opening 39 of vessel 34. Target 32 is positioned in vessel 34, relative to laser 30 and substrate 26, to cause an ablation plume of elemental reagent, formed by ablation of target 32 with laser beam 31, to extend to surface 28 of substrate 26. In one embodiment, target 32 is substantially parallel to, and about four centimeters from, surface 28 of substrate 26.

In one embodiment of the method of the invention, helium, which has been seeded with nitrogen gas, and which is at relatively high pressure, such as about 50 and 300 Torr, is directed through aluminum oxide nozzle 22. Atomic nitrogen beam 24 is formed by exposure of the nitrogen gas to radio frequency (rf) discharge within aluminum oxide nozzle 22 of radio frequency discharge source 20. In one embodiment, the radio frequency discharge supplied to nitrogen passing through aluminum oxide nozzle 22 is sufficient to produce a flux of atomic nitrogen which is greater than about  $10^{18}$  atoms  $\text{sr}^{-1}\text{s}^{-1}$  and having kinetic energies less than about five electron volts. The atomic nitrogen

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beam is directed to surface 28 of substrate 26. Preferably, vacuum source 37 is activated to maintain the absolute pressure with vessel 34 in the range of between about  $1 \times 10^{-7}$  and  $1 \times 10^{-5}$  Torr.

An elemental reagent source is formed, such as by ablation of target 32, which is rotating, as indicated by arrow 42, with laser 30 to form ablation plume 38 of the elemental reagent. In the embodiment wherein the target is graphite, ablation plume 38 includes atomic carbon and carbon chains of various chain lengths.

The atomic nitrogen of the atomic nitrogen source, and the elemental reagent, i.e. elemental carbon, of the elemental reagent source, combine at substrate 24 to react and form extended nitride material 40. When the elemental reagent employed is carbon, the nitride material is a carbon-nitrogen solid film. An "extended nitride material," as that term is employed herein, means a continuous, as opposed to particulate or granular, solid phase. In one embodiment, the extended nitride material includes only a single component, such as  $\beta\text{-C}_3\text{N}_4$ . Alternatively, the extended nitride material includes  $\beta\text{-C}_3\text{N}_4$  and various impurities, such as elemental or molecular impurities. An example of such an impurity is oxygen.

The relative amounts of the atomic nitrogen and elemental reagent which react to form the resulting nitride material can be controlled, for example, by controlling the rate at which the atomic nitrogen source is formed and the relative rate at which the elemental reagent source is formed. In a particularly preferred embodiment, the relative rates at which the atomic nitrogen source and elemental carbon of an



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elemental carbon source are formed causes at least a portion of the resulting extended nitride material, which is formed by reaction of the atomic nitrogen and elemental carbon reagent, to be  $\beta\text{-C}_3\text{N}_4$ .

For example, in one embodiment, the nitrogen gas content in the helium which is subsequently exposed to radio frequency discharge has a concentration in the range of between about one and about twelve percent, by volume, of the combined nitrogen and helium gases. The radio frequency discharge is about one hundred fifty watts, the substrate is Si(100) and the laser employed is a frequency-doubled Quanta Ray GCR-16 laser, that provides eight nanosecond pulses of five hundred and thirty-two nanometer wavelength light with an energy of three hundred millijoules per pulse. A particularly preferred laser is an ultraviolet laser having a wavelength of about one hundred and ninety-three nanometers. Examples of other suitable lasers include: a frequency-tripled Nd-YAG laser emitted a wavelength of about 353 nanometers; a frequency- quadrupled laser emitting a wavelength of about 266 nanometers; a Kr-excimer laser emitting a wavelength of about 146 nanometers; an Xe-excimer laser emitting a wavelength of about 172 nanometers; an XeCl-excimer laser emitting a wavelength of about 318 nanometers; and an Ar-excimer laser emitting a wavelength of about 125 nanometers. The laser output can be shifted by a suitable nonlinear optical technique.

A ten millimeter diameter gaussian output from the laser is focused to a spot on a graphite target surface having a diameter of about two millimeter diameter and at a position off the rotation axis of the target.

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Preferably, the resulting atomic nitrogen beam and the ablation plume accumulate on the substrate, which is heated to a temperature in the range of between about 165 and 600°C by supporting heater 29, to form an extended nitride film having a thickness in the range of between about 0.1 and about five microns.

The invention will now be further and specifically described by the following examples. All parts and percentages are by weight unless otherwise stated.

#### Exemplification

##### Example 1

A pulsed Nd:YAG laser was used to ablate a high-purity graphite target within a stainless steel vacuum chamber. The ablation plume, which contained a variety of carbon fragments, was directed at a diametrically opposed substrate (Si(100) or polycrystalline Ni) located about 4 cm from the target.

An atomic nitrogen beam was formed by a radio frequency (rf) discharge within an  $\text{Al}_2\text{O}_3$  nozzle through which a relatively high pressure ( $\approx 100$  torr)  $\text{N}_2$ -seeded He gas flow passed. This source produced a very high flux of atomic nitrogen ( $\geq 10^{18}$  atomic  $\text{sr}^{-1}\text{s}^{-1}$ ) with kinetic energies in the range of between about 0.1 and one electron volt.

The apparatus shown in Figure 1 was used to prepare a series of carbon nitrogen thin films where the relative flux of atomic nitrogen and substrate temperature were systematically varied during growth. Absolute pressure was maintained in the range of between about  $1 \times 10^{-5}$  and  $1 \times 10^{-4}$  torr during formation of the extended nitride material. In all cases the

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chemical composition of the films was determined with Rutherford backscattering spectroscopy (RBS). Representative RBS data obtained on a series of C-N films grown on Si(100) substrates with a 150 W rf discharge and 1, 4, and 12% N<sub>2</sub> in He are shown in Figure 2.

It was immediately evident upon examination of the RBS data that the fraction of nitrogen in the C-N films increased systematically as the percentage of atomic nitrogen in the atomic beam source was increased from about one to about twelve percent. Quantitative analysis of the RBS data showed that the use of beams with 1, 4, and 12% atomic nitrogen yielded C-N films with average nitrogen contents of 15, 28, and 41%, respectively.

In addition, several experiments were carried out to determine the influence of the source of nitrogen and substrate growth temperature. Importantly, essentially no nitrogen (<1%) was incorporated into films prepared by laser ablation of graphite with the rf-discharge off or in a background of 200 mtorr of N<sub>2</sub>; that is, these films consisted only of amorphous carbon. Hence, the generation and reaction of atomic nitrogen with the elemental carbon and carbon fragments produced by laser ablation was essential to the formation of the C-N films. Secondly, film growth between 165°C and 600°C had little effect on the C:N ratio in the films. These data indicated that within this temperature range, the reaction between laser generated carbon and atomic nitrogen dominated the formation of the C-N materials.

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Data addressing the chemical nature of these C-N materials was also obtained. X-ray photoelectron spectroscopy measurements (XPS) (Surface Science, Model 206) showed that the C-1s and N-1s binding energies in the C-N films were 284.6 and 399.1 eV, respectively. The observed C-1s binding energy was comparable to that observed (284.3) in diamond thin films. More importantly, the observed N-1s binding energy was comparable to that found in molecules with covalent C-N bonds. In contrast, the N-1s binding in boron nitride (a solid in which there was significant charge transfer from boron to nitrogen) was about 1 eV smaller than we observed. The XPS data thus indicated that carbon and nitrogen formed an unpolarized covalent bond in these new C-N materials, and thus our experimental results agreed with earlier theoretical suggestions that there was almost no charge transfer between C and N. The C-N films prepared with the atomic nitrogen source also exhibited excellent adhesion to both Si and Ni substrates, and furthermore, scratch tests indicated that these films were qualitatively hard. In contrast, the C-films obtained from deposition in 200 mTorr of N<sub>2</sub> without atomic nitrogen exhibited poor substrate adhesion and were very soft. Finally, the C-N films also exhibited good thermal stability. RBS analysis of the films after thermal treatments in flowing N<sub>2</sub> up to 800°C showed no observable loss of nitrogen. These characteristics (adhesion, hardness and thermal stability) were all suggestive of extended C-N covalent bonding in the films.

The structure of these new C-N materials was also investigated with electron diffraction. Transmission

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electron microscopy (TEM) studies showed that the films exhibited poor crystallinity, however, small crystallites with grain sizes  $<10$  nm were observed in all of the C-N materials prepared with the atomic nitrogen source. Significantly, relatively sharp electron diffraction ring patterns were observed from the C-N samples, as shown in Figure 3. Control experiments verified that the diffraction peaks were due only to the new C-N materials. First, x-ray fluorescence analyses carried out simultaneously with the electron diffraction measurements demonstrated that there was no substrate (Si or Ni) contamination in material used in the diffraction studies. Secondly, it was not possible to index the experimental diffraction data to diamond or graphite structure (that is, possible impurities) or to Cu or CuO (that is, the TEM support). Lastly, we were unable to observe diffraction rings from the C-films produced in 200 mTorr of  $N_2$ .

Notably, the diffraction patterns obtained from portions of our new C-N materials were indexed to the reflections expected for  $\beta$ - $C_3N_4$ . Six diffraction rings were reproducibly observed in these materials with d-spacings of 2.17, 2.10, 1.24, 1.18, 1.07 and 0.81 Å. The peaks were consistently indexed as the (101), (210), (320), (002), (411), and (611) reflections, respectively, for  $\beta$ - $C_3N_4$ . Furthermore, these experimental d-spacings were in excellent agreement with the values calculated using the theoretical lattice constants for  $\beta$ - $C_3N_4$ : 2.20, 2.11, 1.27, 1.20, 1.09 and 0.80, respectively.

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Taken together, our data provided unambiguous evidence for the presence of  $\beta$ - $C_3N_4$  in these C-N materials. This was also the only crystalline material we identified in the films, regardless of their nitrogen content. This observation suggested that  $\beta$ - $C_3N_4$  was probably the most stable extended C-N solid.

#### Example 2

A pulsed excimer laser (KrF with wavelength 248 nm) was used to ablate graphite within a stainless steel vacuum chamber. The ablation plume was directed at a diametrically opposed substrate of Si (IDO) located about 4 cm from the target.

An atomic nitrogen beam was formed by a radio frequency (rf) discharge within an  $Al_2O_3$  nozzle through which about a 100 torr  $N_2$ -sealed He gas flow passed. This source produced a high flux of atomic nitrogen as described above.

The apparatus shown in Figure 1 was used to prepared carbon-nitrogen films. Absolute pressure was maintained in the range of between about  $1 \times 10^{-5}$  and  $1 \times 10^{-4}$  torr during formation of the extended nitride material. Rutherford backscattering spectroscopy (RBS) analysis of the films showed that the largest average percentage nitrogen in these films was at least 50%.

Transmission electron diffraction analysis of the films indicated good crystallinity, and showed sharp diffraction rings. The diffraction patterns were consistently indexed as the (101), (210), (320), (002), (411) and (611) reflections, respectively, for  $\beta$ - $C_3N_4$ . These data (RBS and electron diffraction) provide unambiguous evidence for the presence of  $\beta$ - $C_3N_4$ .

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Example 3

A pulsed excimer laser (ArF with wavelength 193 nm) was used to ablate graphite within a stainless steel vacuum chamber. The ablation plume was directed at a diametrically opposed substrate of Si (IDO) located about 4 cm from the target.

An atomic nitrogen beam was formed by a radio frequency (rf) discharge within an  $\text{Al}_2\text{O}_3$  nozzle through which about a 100 torr  $\text{N}_2$ -sealed He gas flow passed. This source produced a high flux of atomic nitrogen as described above.

The apparatus shown in Figure 1 was used to prepared carbon-nitrogen films. Absolute pressure was maintained in the range of between about  $1 \times 10^{-5}$  and  $1 \times 10^{-4}$  torr during formation of the extended nitride material. As can be seen in Figure 4, Rutherford backscattering spectroscopy (RBS) analysis of the films showed that the extended nitride material of the film was essentially entirely formed of  $\beta\text{-C}_3\text{N}_4$ .

Example 4

Carbon nitride solids were grown using lasers operating at wavelengths of 532nm (Nd-YAG), 248nm (KrF excimer), and 193nm (ArF excimer) as a function of laser power density using the procedures outlined in Examples 1-3. As the laser power density was decreased the growth rate of the carbon nitride solids decreased (for all three laser wavelengths), but the nitrogen content in the solids increased. At the lowest growth rates studied, 0.5 - 1 Å/second, the nitrogen content ranged from 50-57% irrespective of the laser used as

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determined by RBS. At higher growth rates, the nitrogen content in the carbon nitride solids decreased. These results demonstrated that the growth rate determined the nitrogen content in the carbon nitride solids, and thusly, that other lasers could also be used to generate the reactive carbon fragments used in the apparatus.

In addition, the specific growth rate that gave the optimal (50-57%) nitrogen content in the films depended on the flux of reactive nitrogen produced in the apparatus. When low reactive nitrogen fluxes were produced, optimal composition carbon-nitride solids could be produced if the growth rate was lowered. Correspondingly, when larger reactive nitrogen fluxes were produced, the overall growth rate of optimal (50-57% nitrogen) carbon nitride solids could be increased.

#### Equivalents

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the following claims.



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CLAIMS

1. A composition comprising  $\beta\text{-C}_3\text{N}_4$ .
2. An extended nitride material wherein at least a portion of the material has an empirical formula of  $\beta\text{-C}_3\text{N}_4$ .
2. An extended nitride material of Claim 2 wherein the material is a film.
3. An extended nitride material of Claim 3 wherein at least 10% of the film has an empirical formula of  $\beta\text{-C}_3\text{N}_4$ .
5. An extended nitride material of Claim 3 wherein at least 20% of the film has an empirical formula of  $\beta\text{-C}_3\text{N}_4$ .
6. An extended nitride material of Claim 3 wherein at least 50% of the film has an empirical formula of  $\beta\text{-C}_3\text{N}_4$ .
7. An extended nitride material of Claim 6 wherein the film includes less than about five percent oxygen.
8. An extended nitride material of Claim 3 wherein essentially all of the film has an empirical formula of  $\beta\text{-C}_3\text{N}_4$ .

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9. An extended nitride material of Claim 8 wherein the film has a thickness in the range of between about 0.1 and 5 microns.
10. A composite, comprising:
  - a) a substrate; and
  - b) an extended nitride material on said substrate, at least a portion of said extended nitride material having an empirical formula of  $\beta\text{-C}_3\text{N}_4$ .
11. A composite of Claim 10 wherein the extended nitride material is a film.
12. A composite of Claim 11 wherein the substrate includes silicon.
13. A composite of Claim 11 wherein the substrate includes polycrystalline nickel.
14. A composite of Claim 11 wherein the substrate is a metal.
15. A composite of Claim 14 wherein the substrate is at least one component of a cutting tool.
16. A composite of Claim 14 wherein the substrate includes at least one bearing surface.
17. A composite of Claim 11 wherein essentially all of the film has an empirical formula of  $\beta\text{-C}_3\text{N}_4$ .

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18. A composite of Claim 16 wherein the film has a thickness in a range of between about 0.1 and 5 microns.
19. An extended nitride material wherein at least a portion of said material has an empirical formula of  $\beta\text{-C}_3\text{N}_4$ , the material formed by a method comprising the steps of:
  - a) forming an atomic nitrogen source;
  - b) forming an elemental carbon source, said elemental carbon source including elemental carbon which is reactive with atomic nitrogen of said atomic nitrogen source to form the extended nitride material; and
  - c) combining the atomic nitrogen and the elemental carbon to cause the atomic nitrogen and the elemental carbon to react and form the extended nitride material.
20. A method of forming an extended nitride material, comprising the steps of:
  - a) forming an atomic nitrogen source;
  - b) forming an elemental reagent source, said elemental reagent source including an elemental reagent which is reactive with atomic nitrogen of said atomic nitrogen source to form the extended nitride material; and

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- c) combining the atomic nitrogen and the elemental reagent to cause the atomic nitrogen and the elemental reagent to react and form said extended nitride material.
- 
- 21. A method of Claim 20 wherein the atomic nitrogen source is an atomic nitrogen beam.
  - 22. A method of Claim 21 wherein the atomic nitrogen beam is formed by exposing nitrogen gas to a radio frequency discharge.
  - 23. A method of Claim 22 wherein the elemental reagent is silicon.
  - 24. A method of Claim 22 wherein the elemental reagent is boron.
  - 25. A method of Claim 22 wherein the elemental reagent is carbon.
  - 26. A method of Claim 25 wherein the elemental reagent source is a plume of atomic carbon and carbon chains.
  - 27. A method of Claim 26 wherein the plume is formed by laser ablation of a graphite target.
  - 28. A method of Claim 27 wherein the plume is formed by laser ablation of an oriented pyrolytical graphite target.

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29. A method of Claim 27 wherein the plume is formed by ablating the graphite target with an excimer laser.
30. A method of Claim 29 wherein the excimer laser has a wavelength of about 193 nanometers.
31. A method of Claim 30 wherein the excimer laser is an ArF excimer laser.
32. A method of Claim 29 wherein the excimer laser is a Kr-excimer laser emitting a wavelength of about 146 nanometers.
33. A method of Claim 29 wherein the excimer laser is a Xe-excimer laser emitting a wavelength of about 172 nanometers.
34. A method of Claim 29 wherein the excimer laser is a XeCl-excimer laser emitting a wavelength of about 318 nanometers.
35. A method of Claim 29 wherein the excimer laser is an Ar-excimer laser emitting a wavelength of about 125 nanometers.
36. A method of Claim 29 wherein light waves emitted by the laser are shifted by a nonlinear optical technique.

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37. A method of Claim 28 wherein plume is formed by ablating the graphite target with a Nd:YAG laser.
38. A method of Claim 37 wherein Nd:YAG laser emits a frequency-tripled wavelength of about 353 nanometers.
39. A method of Claim 37 wherein Nd:YAG laser emits a frequency-quadrupled wavelength of about 266 nanometers.
40. A method of Claim 37 wherein the plume is formed by providing about 8 ns laser pulses of about 532 nm light with an energy of about 300 mJ per pulse.
41. A method of Claim 40 wherein the plume and the atomic nitrogen beam are directed at a substrate for formation of the nitride compound on the substrate.
42. A method of Claim 41 wherein the plume and the atomic nitrogen beam are directed at a Si(100) substrate.
43. A method of Claim 41 wherein the plume and the atomic nitrogen beam are directed at a nickel polycrystalline substrate.
44. A method of Claim 41 wherein the relative rates of combination of atomic nitrogen and the elemental reagent from the atomic nitrogen source and the

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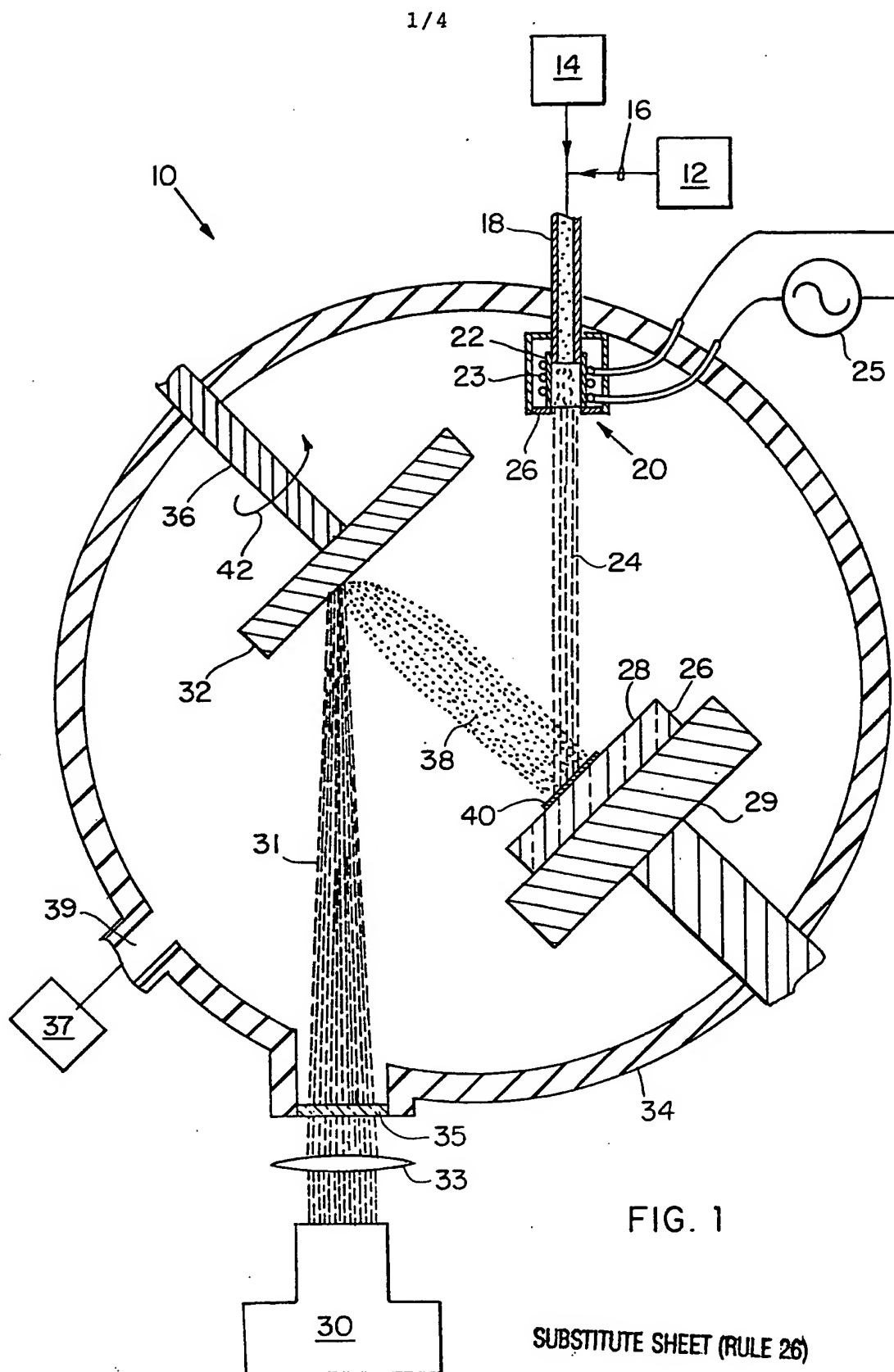
elemental reagent source are sufficient to cause at least a portion of the extended nitride material formed to have an empirical formula of  $\beta$ - $C_3N_4$ .

45. A method of coating  $\beta$ - $C_3N_4$  on a metal substrate, comprising the steps of:
  - a) exposing the metal substrate to an atomic nitrogen source; and
  - b) combining atomic nitrogen of the atomic nitrogen source with elemental carbon at the metal substrate to form said  $\beta$ - $C_3N_4$ .
46. An apparatus for forming an extended nitride material, comprising:
  - a) means for forming an atomic nitrogen source; and
  - b) means for forming an elemental reagent source which is reactive with atomic nitrogen of said atomic nitrogen source to form the extended nitride material.
47. An apparatus of Claim 46 wherein the means for forming the atomic nitrogen source includes a radio-frequency discharge nozzle.
48. An apparatus of Claim 47 wherein the means for forming the elemental reagent source includes a laser and a target.

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49. An apparatus of Claim 48 wherein the elemental target includes graphite.
50. An apparatus of Claim 49 further including a substrate on which the atomic nitrogen and elemental reagent can accumulate as a film of the extended nitride material.





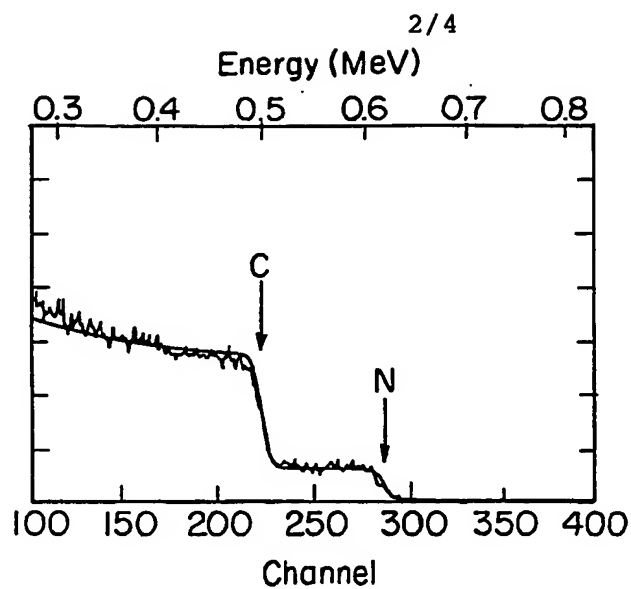


FIG. 2A

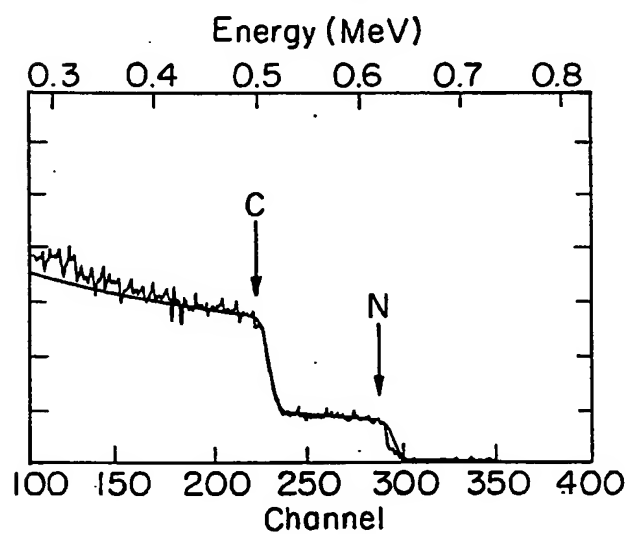


FIG. 2B

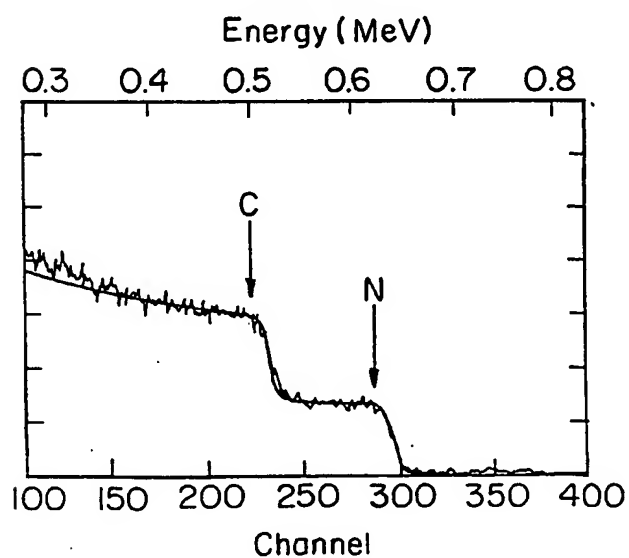


FIG. 2C

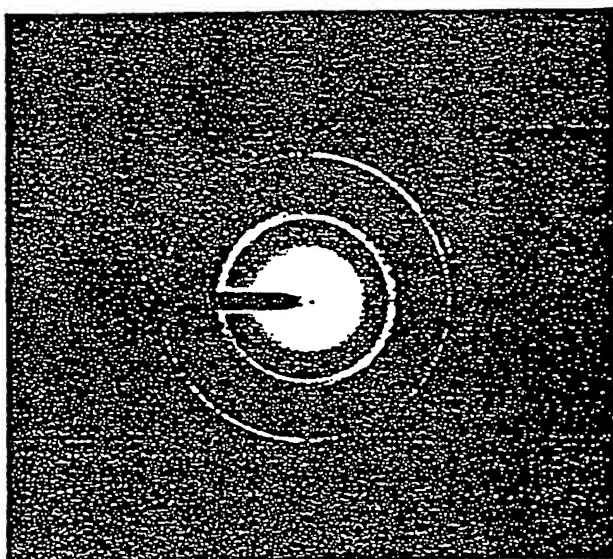


Fig. 3

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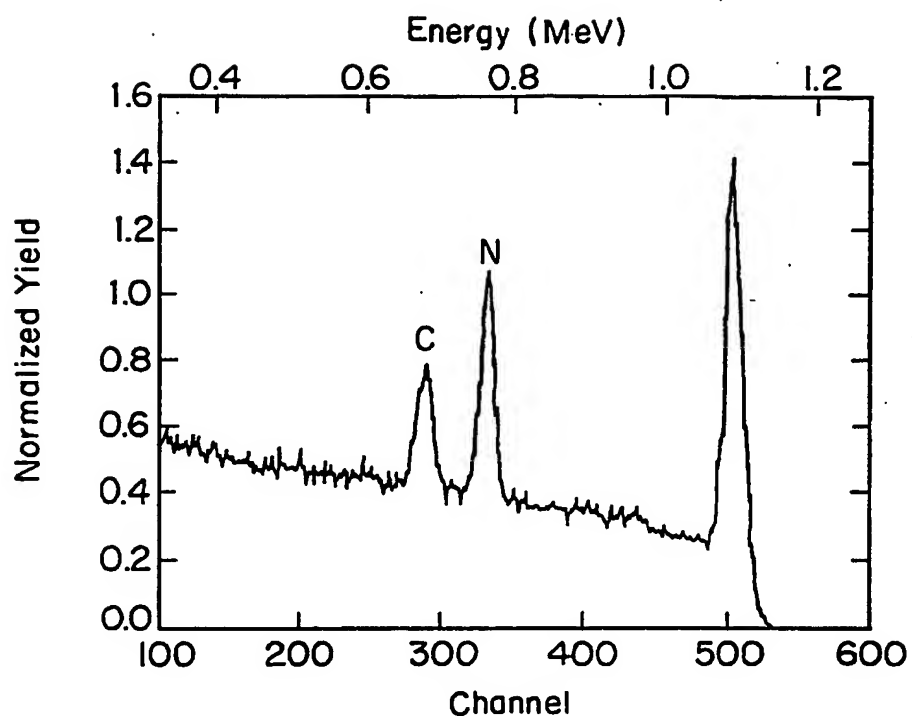


FIG. 4